

**METHOD FOR PRODUCING COMPOSITE PARTICLE AND METHOD FOR
PRODUCING LOADING MATERIAL-ADDED PAPER**

[Claim(s)]

[Claim 1] Carrying out heating stirring, after adding and distributing inorganic particles at a silicic acid alkaline aqueous solution and preparing a slurry. holding solution temperature in the range of 60-100 **, and adding acid -- silica -- a manufacturing method of inorganic particles and a silica composite particle formed by making sol generate and adjusting the pH of the last reaction mixture to a neutral - weak alkaline range.

[Claim 2] A manufacturing method of inorganic particles and the silica composite particle according to claim 1 calcium carbonate, talc, clay, kaolin, calcination kaolin, a titanium dioxide, and aluminium hydroxide of inorganic particles are independent, or they are [silica composite particle] two or more sorts of mixtures.

[Claim 3] A manufacturing method of inorganic particles and the silica composite particle according to claim 1 whose concentration of a silicic acid alkaline aqueous solution is 3 to 10 % of the weight (SiO₂ conversion).

[Claim 4] A manufacturing method of inorganic particles and the silica composite particle according to claim 1 ranges of whose pH of the last reaction mixture by acid addition after distributing inorganic particles to a silicic acid alkaline aqueous solution are 8-11.

[Claim 5] A manufacturing method of loading material containing paper whose loading materials are inorganic particles and the silica composite particle according to claim 1 in a manufacturing method of loading material containing paper by adding a loading material to pulp slurry and milling paper to it.

[Claim 6] A manufacturing method of loading material containing paper to which a loading material makes pulverized coal inorganic particles and the silica composite particle according to claim 1 with a grinder after a drying process in a manufacturing method of loading material containing paper by adding a loading material to pulp slurry and milling paper to it.

[Claim 7] A manufacturing method of claim 1 whose 50% volume mean particle diameter by laser diffraction / the scattering-about method is 10-60 microns - inorganic particles and a silica composite particle given in 6 any 1 paragraphs, and a manufacturing method of loading material containing paper.

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacturing method of the loading material containing paper which has few paper durability falls by loading material internal and in which especially a loft, a whiteness degree, and opacity are high, and the loading material yield is high about the manufacturing method of the paper which carried out internal [of the manufacturing method of a new compound loading material, and the loading material].

[0002]

[Description of the Prior Art] In recent years, the weight saving of paper is needed from the standpoint of the environmental impact mitigation including forest-resources protection, a saving-resources problem, and a waste problem. Especially, when aiming at the weight saving of paper, in order to improve a whiteness degree, opacity, and a printability, internal [of various kinds of loading materials] is carried out, and they are manufactured in the field of printing paper, wrapping paper, etc. The method and clay which carry out internal [of the loading material with a big refractive index like a titanium dioxide as the whiteness degree of the paper by loading material internal and the opaque improvement method] from the former, and raise scattering efficiency, Internal [of the loading material of the refractive-index 1.5 neighborhoods, such as talc, calcium carbonate, and an organic color,] is carried out, and the method which controls adhesion between pulp fibers and to which dispersion surface area is made to increase is taken.

[0003] In order to correspond to the weight saving of paper, methods, such as only lowering basis weight or raising the ratio of deinking pulp, have been performed until now. However, by this method, paper becomes thin, a whiteness degree and opacity fall and printabilities, such as a strike-through, worsen. Opacity and a strike-through have a close relation to the thickness of paper, and bulky paper has been manufactured until now by using pulp too much or using the pulp out of which Takashi comes.

[0004]

[Problem(s) to be Solved by the Invention] However, most flowed out into Shiramizu at the time of paper making, and loading materials, such as calcium carbonate with the above small particle diameter, had the problem that maintenance into paper was very bad. Such small loading material particles have a fault which checks combination between textiles and in which paper durability is reduced by being distributed between pulp fibers.

[0005] Interfiber bonding is not checked by the loading material particles whose

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purposes of this invention improve the yield of a loading material and **which** are distributed between textiles, It is providing the manufacturing method and **loading** material containing paper of a bulky loading material whose manufacture of "**the light and thick paper**" which can take out ** also with a small amount of pulp, **and** can improve a whiteness degree and opacity simultaneously from it is enabled.

[0006]

[Means for Solving the Problem]Carrying out heating stirring of it, **after** an aforementioned problem adds and distributes inorganic particles at a **silicic acid** alkaline aqueous solution and prepares a slurry. holding solution temperature in the range of 60-100 **, and adding acid -- silica -- by making sol generate and **adjusting** the pH of the last reaction mixture to a neutral - weak alkaline range, inorganic particles and a silica composite particle were manufactured, and it was solved by **carrying out** internal to pulp slurry as a loading material.

[0007]

[Embodiment of the Invention]the about several nanometers silica generated **when** this invention adds acid, such as dilute sulfuric acid, in a specific silicate solution -- sol -- particles being made to adhere to the whole surface of inorganic particles **thinly**, and, silica -- following on the crystal growth of sol -- the silica on a non-subtlety particle surface -- sol -- the silica on a non-subtlety particle surface different from particles -- sol -- combination arises among particles and the floc of inorganic particles and a silica composite particle is formed

[0008]For this reason, the pH of the last reaction mixture is an important factor, and it is necessary to make pH into the neutral - weak alkaline range, and it is necessary to control pH so that hydration silicic acid (white carbon) does not generate to the system of reaction. The ranges of desirable pH are 8-11. if sulfuric acid is added until pH becomes less than seven acid conditions -- silica, since not sol but white carbon generates and white carbon encloses the surroundings of the floc of inorganic particles spherically, The optical characteristic of white carbon appears preferentially and the optical characteristic of inorganic particles incore is no longer demonstrated at all. the case where pH exceeds 11 -- silica -- generating of sol becomes insufficient -- the floc of the inorganic particles and silica composite of this invention -- obtaining -- a stake.

[0009]the silica generated during a reaction by this invention -- sol is a silica sol particle with a particle diameter of 10-20 nm which makes react to the diluent of mineral acid, such as sulfuric acid, chloride, and nitric acid, under an elevated temperature by using a specific silicate (water glass) as a raw material, and is obtained by a hydrolysis reaction and polymerization-ization of silicic acid.

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[0010]Although the silicic acid alkali solution in particular used by this invention is not limited, a specific silicate solution (the No. 3 water glass) is desirable in respect of availability. 3 to 10 % of the weight is preferred for the concentration of a silicic acid alkali solution at a part for silicic acid in solution (SiO_2 conversion). Not inorganic particles and silica compound floc but the aforementioned inorganic particles will be encapsulated by white carbon, and, as for the complex which will be formed if it exceeds 10 % of the weight, the optical characteristic of inorganic particles in core will no longer be demonstrated at all. At less than 3 % of the weight, since the silica components in a composite particle fall, it becomes difficult to form an aggregate particle.

[0011]As inorganic particles used by this invention, precipitated calcium carbonate, heavy calcium carbonate, talc, kaolin, clay, calcination kaolin, a titanium dioxide, aluminium hydroxide, etc. which are the loading materials for paper making are mentioned. As particle diameter, 0.05-50 microns is desirable in view of the particle diameter of the compound aggregate particle formed.

[0012]Since a specific silicate solution has a function as a dispersing agent, these inorganic particles are used after distributing in a specific silicate solution beforehand. However, when the dispersibility of particles is not good when distributing, after distributing a loading material in the water which added the dispersing agent, adding after mixing of the specific silicate solution may be carried out. It is more desirable to use a dispersing agent, since especially a titanium dioxide tends to condense particle diameter small. As a dispersing agent, sodium hexametaphosphate, sodium pyrophosphate, polycarboxylic acid soda, etc. are mentioned.

[0013]Although the above-mentioned inorganic particles may be used alone, they can also manufacture the high compound loading material of functionality by using together two or more sorts of inorganic particles.

[0014]Although the diluent of mineral acid, such as dilute sulfuric acid, dilute hydrochloric acid, and aqua fortis, acetic acid, carbon dioxide, etc. are mentioned as acid used by this invention, dilute sulfuric acid is the most desirable in respect of a price and handling. The concentration at the time of the addition in the case of using dilute sulfuric acid has desirable 0.2 - 1.0 molar concentration.

[0015]About the reaction temperature at the time of manufacture of the inorganic particles and silica composite particle in this invention, the range of 60-100 °C is desirable. reaction temperature -- silica -- generation of sol, the rate of crystal growth, and the formed dynamic strength of inorganic particles and a silica compound aggregate particle are affected. reaction temperature -- less than 60 °C -- silica -- generation and the growth rate of sol are slow, and since the bond strength of the formed inorganic

particles and silica compound aggregate particle is weak, floc breaks easily in **Hy Schar** who takes at the time of paper milling of loading material containing paper. If **it** exceeds 100 **, a reaction process will become complicated in order to have to use **autoclave**, since it is a drainage system reaction. Optimum reaction temperature is 70-90 **.

[0016]When manufacturing inorganic particles and a silica composite particle, inorganic particles are added to a silicic acid alkaline aqueous solution, it **distributes**, and a slurry is prepared, but as for this slurry concentration, 3 to 35 % of the **weight** is desirable. By adjusting slurry concentration, the composition ratio of inorganic particles and silica is decided at the same time the particle diameter of the inorganic particles and silica compound aggregate particle formed is controlled.

[0017]It is possible by making mean particle diameter of inorganic particles and a silica compound aggregate particle into the large diameter of 10-60 microns to raise the yield of a loading material. The following three methods are mentioned as the method of particle diameter control. ** Carry out loading material slurry concentration produced by adding inorganic particles to the silicic acid alkaline aqueous solution of concentration 3.61% as a part for silicic acid to 3.2 to 9.6% of the weight. ** Use a 2-10-micron inorganic particle with large particle diameter as a raw material. ** the solid which can obtain the slurry of inorganic particles and a silica compound aggregate particle by being air-dry or carrying out stoving -- dry type -- or carry out wet milling. It is possible to carry out particle diameter control by the above method at the size of 10-60 microns.

[0018]Stirring, after adding and distributing inorganic particles at a silicic acid alkaline aqueous solution and preparing a slurry in this invention. holding solution temperature in the range of 60-100 **, and adding acid -- silica -- sol is made to generate, inorganic particles and a silica composite particle are manufactured for the pH of the last reaction mixture neutrality - alkalescence, and by adjusting to the range of 8-11 preferably, and a wet cake will be obtained if a slurry is filtered and rinsed.

[0019]Again, it distributes in water, this wet cake is made into a loading material slurry, internal [of this] is carried out to pulp slurry at the time of paper milling, and loading material containing paper is obtained. After making the wet cake of inorganic particles and a silica composite particle into dry particles by air-drying or stoving processing at this time, a dry mill or a wet grinding mill is used again, If internal [of the loading material slurry which adjusted particle diameter] is carried out to pulp slurry at the time of paper milling and loading material containing paper is obtained, it is possible to improve the loft which is an effect of this invention by leaps and bounds. As a wet grinding mill, a publicly known homomixer, a homogenizer, a Sand grinder, etc. are

mentioned.

[0020]In this invention, in the range which does not spoil the effect of this invention, as a publicly known loading material Clay, The organic loading material manufactured from synthetic resins, such as inorganic loading materials, such as silica, talc, calcination kaolin, and calcium carbonate, or vinyl chloride resin, polystyrene resin, urea formaldehyde resin, melamine system resin, styrene / butadiene series copolymer system resin, can also be used together.

[0021]If needed Polyacrylamide system polymers, polyvinyl alcohol system polymers, Paper reinforcing agents, such as cation-ized starch, urea/formalin resin, melamine/formalin resin; The salt of the copolymer of acrylamide / aminomethyl acrylamide, Filterability or yield improvers, such as cation-ized starch, polyethyleneimine, polyethylene oxide, acrylamide / sodium acrylate copolymer; auxiliary agents, such as aluminum sulfate (sulfuric acid band), a water resistance-ized agent, ultraviolet inhibitor, and a fading inhibitor, etc. may be contained.

[0022]

[Example]Hereafter, although this invention is explained in detail according to an example and a comparative example, this invention is not limited to these. Percent shows mass percent during explanation.

[0023]About the neutral paper of fine quality manufactured by the example and the comparative example, a loft, a whiteness degree, opacity, breaking length, and the loading material yield were measured by the method shown below.

- Loft : the density of paper was computed from basis weight and thickness of paper. It is shown that a loft is so high that it is low-density.
- Measurement of a whiteness degree : the whiteness degree was measured with hunter white chromoscope based on JIS P 8123.
- Measurement of opacity : opacity was measured using the hunter reflectometer based on JIS P 8138.
- Yield of a loading material : after cutting off ten 10x10-cm pieces of paper and drying them for 105 °C x 3 hours from the hand papermaking sheet which blended the hand papermaking sheet (blank) and loading material which were created beforehand, and which have not blended the loading material, they are **** and ** about oven dry weight. Next, it asks for the ash contained in a sheet by burning this bone-dry piece of paper with an electric furnace for 575 °C x 2 hours. The loading material yield (%) was computed from the following formula.

Loading-material yield = {(the sheet ash weight containing a loading material / said oven-dry-weight-blank ash weight / the oven dry weight)} / loading-material

compounding-rate x100 and breaking length: It asked with the following formula by JIS P 8113.

Breaking-length = tensile strength / (basis weight of the width x specimen of a specimen) x1000, and ash: Based on JIS P 8128, ashing temperature was 575 **.

- The ratio of a composite particle : the ingredient ratio of the composite particle was measured by X-ray fluorescence.

Comprehensive quality evaluation was performed in the above measurement result. Evaluation was made into the following three-stage.

O : it is dramatically good. : It is good. x: It is inferior. [0024]The granular material 30g of the <synthetic example 1> calcium carbonate (product TPmade from Okutama industry-121) was added to 312 g of sodium silicate solutions (it is considered as a part for silicic acid, and is 3.61%), distributed processing was performed for 20 minutes at the number of rotations of 3000 rpm using the homomixer, and the calcium carbonate slurry was prepared. Next, temperature up was carried out to 75 ** with the oil bath, having put this slurry into the four-lot flask of 1L to which the agitator, the thermo sensor, and the reflux condenser were attached, and stirring it. Next, keeping the slurry in a container at 75 **, the micro tuning pump was used, 0.36 N of sulfuric acid 276g was dropped over 3 hours by a part for 1.53-ml/in dropping speed, and calcium carbonate silica compound floc was obtained. The pH of the reaction mixture at this time was 10.3. The wet cake of calcium carbonate silica compound floc was obtained filtration and by rinsing and filtering again using the No.2 filter paper. When the size distribution measuring device master sizer S (made in Malvern) was used and volume mean particle diameter was measured 50% by laser diffraction / the scattering-about method, mean particle diameter was 8 microns and the ratio of calcium carbonate and silica was 70:30.

[0025]In the example 1 of the <synthetic example 2> composition, calcium carbonate silica compound floc was obtained like the synthetic example 1 except having changed the granular material of calcium carbonate (product TPmade from Okutama industry-121) into 70 g. The pH of the reaction mixture at this time was 10.2. The mean particle diameter of the obtained calcium carbonate silica compound floc was 5.4 microns, and the ratio of calcium carbonate and silica was 86:14.

[0026]In the example 1 of the <synthetic example 3> composition, stoving was performed for the obtained calcium carbonate silica compound floc in 105 ** and 5 hours. Next, in this dried powder object, the Sand grinder performed wet milling and the calcium carbonate silica compound floc whose mean particle diameter is 2.0 microns was obtained.

[0027]The granular material 18g and 12 g of titanium dioxides (FURUKAWA FA-50) of the <synthetic example 4> calcium carbonate (product TPmade from Okutama industry-121) are added to 312 g of sodium silicate solutions (it is considered as a part for silicic acid, and is 3.61%), For 20 minutes and distributed processing were performed at the number of rotations of 3000 rpm using the homomixer, and the mixed slurry of calcium carbonate and a titanium dioxide was prepared. Next, temperature up was carried out to 75 ** with the oil bath, having put this slurry into the four-lot flask of 1L to which the agitator, the thermo sensor, and the reflux condenser were attached, and stirring it. Next, keeping the slurry in a container at 75 **, the micro tuning pump was used, 0.36 N of sulfuric acid 276g was dropped over 3 hours by a part for 1.53-ml/in dropping speed, and calcium carbonate and titanium dioxide silica compound floc were obtained. The pH of the reaction mixture at this time was 10.1. The wet cake of calcium carbonate and titanium dioxide silica compound floc was obtained filtration and by rinsing and filtering again using the No.2 filter paper. Mean particle diameter was 4.9 microns and the ratio of calcium carbonate, a titanium dioxide, and silica was 52:34:14.

[0028]The granular material 30g of the <synthetic example 5> kaolin (product made from CADAM Amazon 88SD) was added to 312 g of sodium silicate solutions (it is considered as a part for silicic acid, and is 3.61%), distributed processing was performed for 20 minutes at the number of rotations of 3000 rpm using the homomixer, and the kaolin slurry was prepared. Next, temperature up was carried out to 75 ** with the oil bath, having put this slurry into the four-lot flask of 1L to which the agitator, the thermo sensor, and the reflux condenser were attached, and stirring it. Next, keeping the slurry in a container at 75 **, the micro tuning pump was used, 0.36 N of sulfuric acid 276g was dropped over 3 hours by a part for 1.53-ml/in dropping speed, and kaolin silica compound floc was obtained. The pH of the reaction mixture at this time was 8.5. The wet cake of kaolin silica compound floc was obtained filtration and by rinsing and filtering again using the No.2 filter paper. Mean particle diameter was 12.7 microns and the ratio of kaolin and silica was 70:30.

[0029]In the example 5 of the <synthetic example 6> composition, stoving was performed for the obtained kaolin silica compound floc in 105 ** and 5 hours. Next, in this dried powder object, the Sand grinder performed wet milling and the kaolin silica compound floc whose mean particle diameter is 2.5 microns was obtained.

[0030]In the example 1 of the <synthetic example 7> composition, calcium carbonate silica compound floc was obtained like the synthetic example 1 except having changed the granular material of calcium carbonate into 20 g. The pH of the reaction mixture at this time was 10.2. The mean particle diameter of the obtained calcium carbonate silica

compound floc was 10.0 microns, and the ratio of calcium carbonate and silica was 65:35.
 [0031]In the example 1 of the <synthetic example 8> composition, calcium carbonate silica compound floc was obtained like the synthetic example 1 except having changed the granular material of calcium carbonate into 10 g. The pH of the reaction mixture at this time was 10.1. The mean particle diameter of the obtained calcium carbonate silica compound floc was 30.5 microns, and the ratio of calcium carbonate and silica was 60:40.

[0032]In the example 5 of the <synthetic example 9> composition, kaolin silica compound floc was obtained like the synthetic example 5 except having changed the granular material of kaolin into 20 g. The pH of the reaction mixture at this time was 9.8. The mean particle diameter of the obtained kaolin silica compound floc was 15.0 microns, and the ratio of kaolin and silica was 70:30.

[0033]In the example 5 of the <synthetic example 10> composition, kaolin silica compound floc was obtained like the synthetic example 5 except having changed the granular material of kaolin into 10 g. The pH of the reaction mixture at this time was 9.6. The mean particle diameter of the obtained kaolin silica compound floc was 35.5 microns, and the ratio of kaolin and silica was 68:32.

[0034]The granular material 30g of the <synthetic example 11> calcium carbonate (product TPmade from Okutama industry-121) was added to 312 g of sodium silicate solutions (it is considered as a part for silicic acid, and is 3.61%), distributed processing was performed for 20 minutes at the number of rotations of 3000 rpm using the homomixer, and the calcium carbonate slurry was prepared. Next, temperature up was carried out to 75 ** with the oil bath, having put this slurry into the four-lot flask of 1L to which the agitator, the thermo sensor, and the reflux condenser were attached, and stirring it. Next, keeping the slurry in a container at 75 **, the micro tuning pump was used, the sulfuric acid 180g of 10% of the weight of concentration was dropped over 3 hours by a part for 1.0-ml/in dropping speed, and the calcium carbonate silica composite particle was obtained. The pH of the reaction mixture at this time was 5.7. The wet cake of the calcium carbonate silica composite particle was obtained filtration and by rinsing and filtering again using the No.2 filter paper. Mean particle diameter was 9 microns, the ratio of calcium carbonate and silica was 25:75 and its ratio of silica was higher than calcium carbonate. When the composite particle was observed with the electron microscope, particles are spherical and calcium carbonate was thoroughly covered by white carbon.

[0035]The granular material 30g of the <synthetic example 12> kaolin (product made from CADAM Amazon 88SD) was added to 312 g of sodium silicate solutions (it is considered as a part for silicic acid, and is 3.61%), distributed processing was performed

for 20 minutes at the number of rotations of 3000 rpm using the homomixer, and the kaolin slurry was prepared. Next, temperature up was carried out to 75 °C with the oil bath, having put this slurry into the four-lot flask of 1L to which the agitator, the thermo sensor, and the reflux condenser were attached, and stirring it. Next, keeping the slurry in a container at 75 °C, the micro tuning pump was used, the sulfuric acid 180g of 10% of the weight of concentration was dropped over 3 hours by a part for 1.0-ml/in dropping speed, and the kaolin silica composite particle was obtained. The pH of the reaction mixture at this time was 6.5. The wet cake of the kaolin silica composite particle was obtained filtration and by rinsing and filtering again using the No.2 filter paper. Mean particle diameter was 9.5 microns, the ratio of kaolin and silica was 20:80 and its ratio of silica was higher than kaolin. When the composite particle was observed with the electron microscope, particles are spherical and kaolin was thoroughly covered by white carbon.

[0036][Example 1] To the slurry (concentration 1.00%) of hardwood bleached pulp (LBKP CSF407ml), the compound aggregate particle slurry of the synthetic example 1 was added so that it might become 10% per pulp oven dry weight, and to it, the sulfuric acid band was added 1% per oven dry weight after stirring for 1 minute. For 1 minute, as a yield improvement agent, 100 ppm addition stirring per sum total oven dry weight of pulp and a loading material of the cation Pulse Amplitude Modulation (HAIMO lock DR-1500) was carried out, and after stirring, a little sulfuric acid bands were added so that pH might be set to 8.0-8.5. Using this pulp slurry that carried out preparation, paper was milled so that target basis weight might serve as 64g/m² and Kaminaka ash might be 10 % of the weight with a square-shaped extract machine, and it dried after drying and with an air blasting dryer (50 °C, 1 hour) with a press, and the sheet sample was produced. The density of this sheet, a whiteness degree, opacity, and breaking length were measured, and it was shown in Table 1.

[0037][Example 2] In Example 1, the sheet was produced on the same conditions except having used the compound floc of the synthetic example 2. Measurement evaluation of the physical properties was carried out like acquired Example 1 with a sheet, and the result was shown in Table 1.

[0038][Example 3] In Example 1, the sheet was produced on the same conditions except having used the compound floc of the synthetic example 3. Measurement evaluation of the physical properties was carried out like acquired Example 1 with a sheet, and the result was shown in Table 1.

[0039][Example 4] In Example 1, the sheet was produced on the same conditions except having used the compound floc of the synthetic example 4. Measurement evaluation of

the physical properties was carried out like acquired Example 1 with a sheet, and the result was shown in Table 1.

[0040][Comparative example 1] In Example 1, the sheet was produced on the same conditions except having used the granular material of calcium carbonate (product TPmade from Okutama industry-121). Measurement evaluation of the physical properties was carried out like acquired Example 1 with a sheet, and the result was shown in Table 1.

[0041][Comparative example 2] In Example 1, the sheet was produced on the same conditions except having used the composite particle of the synthetic example 11. Measurement evaluation of the physical properties was carried out like acquired Example 1 with a sheet, and the result was shown in Table 1.

[0042][Example 5] In Example 1, the sheet was produced on the same conditions except having used the compound floc of the synthetic example 5. Measurement evaluation of the physical properties was carried out like acquired Example 1 with a sheet, and the result was shown in Table 1.

[0043][Example 6] In Example 1, the sheet was produced on the same conditions except having used the compound floc of the synthetic example 6. Measurement evaluation of the physical properties was carried out like acquired Example 1 with a sheet, and the result was shown in Table 1.

[0044][Comparative example 3] In Example 1, the sheet was produced on the same conditions except having used kaolin (product made from CADAM Amazon 88SD). Measurement evaluation of the physical properties was carried out like acquired Example 1 with a sheet, and the result was shown in Table 1.

[0045][Comparative example 4] In Example 1, the sheet was produced on the same conditions except having used the composite particle of the synthetic example 12. Measurement evaluation of the physical properties was carried out like acquired Example 1 with a sheet, and the result was shown in Table 1.

[0046]The physical-properties measurement evaluation result of the above Examples 1-6 and the comparative examples 1-4 was shown in Table 1.

[0047][Example 7] To the slurry (concentration 1.00%) of hardwood bleached pulp (LBKP CSF407ml), the compound aggregate particle slurry of the synthetic example 7 was added so that it might become 10% per pulp oven dry weight, and to it, the sulfuric acid band was added 1% per oven dry weight after stirring for 1 minute. For 1 minute, as a yield improvement agent, 100 ppm addition stirring per sum total oven dry weight of pulp and a loading material of the cation Pulse Amplitude Modulation (HAIMO lock DR-1500) was carried out, and after stirring, a little sulfuric acid bands were added so

that pH might be set to 8.0-8.5. Using this pulp slurry that carried out preparation, paper was milled so that target basis weight might serve as 64 g/m² and Kaminaka ash might be 10 % of the weight with a square-shaped extract machine, and it dried after drying and with an air blasting dryer (50 **, 1 hour) with a press, and the sheet sample was produced. The density of this sheet, a whiteness degree, opacity, breaking length, and the loading material yield were measured, and it was shown in Table 2.

[0048][Example 8] In Example 7, the sheet was produced on the same conditions except having used the compound floc of the synthetic example 8. Measurement evaluation of the physical properties was carried out like acquired Example 7 with a sheet, and the result was shown in Table 2.

[0049][Example 9] In Example 7, the sheet was produced on the same conditions except having used the compound floc of the synthetic example 9. Measurement evaluation of the physical properties was carried out like acquired Example 7 with a sheet, and the result was shown in Table 2.

[0050][Example 10] In Example 7, the sheet was produced on the same conditions except having used the compound floc of the synthetic example 10. Measurement evaluation of the physical properties was carried out like acquired Example 7 with a sheet, and the result was shown in Table 2.

[0051]The physical-properties measurement evaluation result of the above Examples 7-10 and the comparative examples 1 and 2 was shown in Table 2.

[0052]

[Table 1]

表1

	無機微粒子	pH	複合粒子粒径 μm	複合粒子組成 無機微粒子/シリカ	サトクラインダー	坪量 g/m ²	紙厚 μm	密度 g/m ³	灰分 %	白色度 %	不透明度 %	裂断長 km	総合評価
実施例 1	炭酸カルシウム	10.3	8	70/30		65.0	138	0.47	10.1	88.3	86.2	1.9	○
実施例 2	炭酸カルシウム	10.2	5.4	86/14		65.1	142	0.46	10.2	88.5	86.3	1.9	○
実施例 3	炭酸カルシウム	10.3	2	70/30	実施例1の複合粒子を処理	65.5	150	0.44	10.1	89.1	86.9	2.2	◎
実施例 4	炭酸カルシウム/TiO ₂	10.1	4.9	52/34/14		65.2	142	0.46	10.1	90.0	88.0	2.2	◎
比較例 1	炭酸カルシウム					65.3	133	0.48	10.2	87.5	85.5	1.5	×
比較例 2	炭酸カルシウム	5.7	9	25/75		65.1	130	0.50	10.3	87.1	84.1	1.4	×
実施例 5	シリカ	8.5	12.7	70/30		65.0	141	0.46	10.0	88.2	86.0	2.1	○
実施例 6	シリカ	8.5	2.5	70/30	実施例5の複合粒子を処理	65.1	148	0.44	10.2	88.5	86.5	2.2	◎
比較例 3	シリカ					65.2	130	0.50	10.1	85.0	84.1	1.5	×
比較例 4	シリカ	6.5	9.5	20/80		65.3	126	0.52	10.2	84.8	83.1	1.4	×

[0053]As shown in Table 1, in the calcium carbonate silica composite particle which manufactured calcium carbonate of Example 1 and Example 2 as a raw material, as compared with the case of only calcium carbonate of the comparative example 1, the density of paper was falling 4 to 6%, and the loft was accepted. 0.8 to 1.0 point, opacity

was rising 0.7 to 0.8 point, breaking length also became high 27%, and the whiteness degree had few falls of the paper durability by loading material internal.

[0054]In what ground the calcium carbonate silica composite particle in which Example 3 carried out stoving with the Sand grinder, the density of paper was falling 10% and the very high loft was accepted. 1.6 point, opacity was rising 1.3 point, breaking length also became high 47%, and the whiteness degree had very few falls of paper durability.

[0055]In calcium carbonate and the titanium dioxide silica composite particle of Example 4, the density of paper was falling 6% and the high loft was accepted. Since the titanium dioxide was composite-ized, a whiteness degree and opacity were rising 2.5 point, breaking length also became high 47%, and there were very few falls of paper durability.

[0056]By what was made into the acidic regions of 5.7, the pH of the last reaction mixture of the comparative example 2. The ratio of silica of the ratio of calcium carbonate and silica was higher than calcium carbonate at 25:75, since calcium carbonate was the spherule thoroughly covered by white carbon, there is no loft and opacity fell [the whiteness degree] 1.4 point 0.4 point. Breaking length is almost changeless.

[0057]In the kaolin silica composite particle which manufactured kaolin of Example 5 as a raw material, as compared with the case of only kaolin of the comparative example 3, the density of paper was falling 8% and the high loft was accepted. 1.2 point, opacity was rising 1.9 point, breaking length also became high 40%, and the whiteness degree had few falls of paper durability.

[0058]In what ground the kaolin silica composite particle in which Example 6 carried out stoving with the Sand grinder, as compared with the case of only kaolin of the comparative example 3, the density of paper was falling 12% and the high loft was accepted. 1.5 point, opacity was rising 2.4 point, breaking length also became high 47%, and the whiteness degree had few falls of paper durability.

[0059]By what was made into the acidic regions of 6.5, the pH of the last reaction mixture of the comparative example 4. The ratio of kaolin and silica is 20:80, the ratio of silica is higher than kaolin, since kaolin is the spherule thoroughly covered by white carbon, there is no loft, and whiteness degrees are 0.2 point and opacity. It fell 1.0 point. Breaking length is almost changeless.

[0060]

[Table 2]

表2

	無機微粒子	pH	複合粒子粒径 μm	複合粒子組成 無機微粒子/シリカ	サトウライナー	坪量 g/m ²	紙厚 μm	密度 g/m ³	灰分 %	白度 %	不透明度 %	裂断長 km	塩料歩留まり %	総合評価
実施例 7	炭酸カルシウム	10.2	10	65/35		65.3	145	0.45	10.2	88.2	88.1	1.9	45	◎
実施例 8	炭酸カルシウム	10.1	30.5	60/40		65.1	141	0.46	10.3	88.3	88.2	2.0	47	◎
実施例 9	シリカ	9.8	15	70/30		65.2	142	0.46	10.1	86.3	86.1	2.2	43	◎
実施例 10	シリカ	9.8	35.5	68/32		65.4	143	0.46	10.4	86.4	86.3	2.1	45	◎
比較例 1	炭酸カルシウム					65.3	133	0.49	10.2	87.5	85.5	1.5	22	×
比較例 2	炭酸カルシウム	5.7	9	25/75		65.2	130	0.50	10.1	85.0	84.1	1.5	24	×

[0061]As shown in Table 2, when the particle diameter of the composite particle of Examples 7-10 was 10 microns or more, a loft, a whiteness degree, and opacity were

high, there were also few falls of paper durability and their loading material yield was dramatically high at 43 to 47%.

[0062]

[Effect of the Invention]Carrying out heating stirring, after adding and distributing inorganic particles at a silicic acid alkaline aqueous solution and preparing a slurry. holding solution temperature in the range of 60-100 **, and adding acid -- silica -- sol was made to generate and loading material containing paper provided with the following characteristics was obtained by carrying out internal [of the inorganic particles and the silica composite particle formed by adjusting the pH of the last reaction mixture to the neutral - weak alkaline range] to paper.

1) 3 [excellent in optical properties from which the high paper of a light and thick loft is obtained, such as two whiteness degree and opacity,] -- though it is bulky, the yield of four loading material excellent in paper durability (breaking length, tearing strength) is high

Abstract:

PROBLEM TO BE SOLVED: To obtain a bulky loading material improving yielding percentage, capable of expressing bulkiness with a little pulp without inhibited interfiber bondings caused by loading material particles distributed among the fibers and simultaneously improving whiteness and opacity and provide loading material-added paper.

SOLUTION: Inorganic fine particle-silica composite particles are produced by adding and dispersing the inorganic particles in an aqueous alkali silicate solution to prepare a slurry, subsequently heating and agitating the slurry and adding an acid while keeping the temperature of the slurry at 60-100°C to produce a silica sol and adjusting the pH of the final reaction solution in the range of a neutral to a weak alkaline value. Paper is produced by adding the same as a loading material inside a pulp slurry.